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(54) Title: ELASTOMERIC COMPOSITION

(57) Abstract: The present invention is a composition including an isobutylene-based copolymer and polybutene. The copolymers may be mixed with an exfoliating compound and clay, the entire composition forming a nanocomposite. The clay may or may not have an additional exfoliating treatment present prior to mixing with the interpolymers. The composition of the invention has improved air barrier properties and processing properties, and is suitable as an air barrier. One embodiment of the invention is an elastomeric composition including at least one random copolymer of at least a C₄ to C₇ isomonoolefin derived unit, at least one filler, and polybutene oil having a number average molecular weight greater than 400. The copolymer may be selected from a halogenated poly(isobutylene-*co-p*-methylstyrene), a halogenated star-branched butyl rubber, or a halogenated butyl rubber, and mixtures thereof.



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TITLE: ELASTOMERIC COMPOSITION**FIELD OF THE INVENTION**

The present invention is directed towards a low-permeability elastomeric composition which may include a nanoclay, and more particularly to a composition of an isobutylene-based copolymer with a filler such as carbon black and clay with polybutene processing oil to form an air barrier such as a tire innerliner.

BACKGROUND

Bromobutyl and chlorobutyl rubbers are the polymers of choice for air-retention in tubeless tires. Similarly, brominated poly(isobutylene-*co-p*-methylstyrene) (BIMS), such as disclosed in US 5,162,445 and 5,698,640, is typically used when heat resistance or another important property is of importance. The selection of ingredients for the commercial formulations of elastomers depends upon the balance of properties desired and the application and end use. For example, in the tire industry, processing properties of the green (uncured) compound in the tire plant versus in-service performance of the cured rubber tire composite, and the nature of the tire, i.e. bias versus radial tire, and passenger versus truck versus aircraft tire are all important considerations that must be balanced.

One method to alter product properties and improve air barrier properties is to add clays to elastomers to form a "nanocomposite". Nanocomposites are polymer systems containing inorganic particles with at least one dimension in the nanometer range. Some examples of these are disclosed in US 6,060,549, 6,103,817, 6,034,164, 5,973,053, 5,936,023, 5,883,173, 5,807,629, 5,665,183, 5,576,373, and 5,576,372. A common type of inorganic particle used in nanocomposites are phyllosilicates, an inorganic substance from the general class of so called "nano-clays" or "clays". Ideally, intercalation should take place in the

nanocomposite, wherein the polymer inserts into the space or gallery between the clay surfaces. Ultimately, it is desirable to have near complete exfoliation, wherein the polymer is fully dispersed with the individual nanometer-size clay platelets. Due to the general enhancement in air barrier qualities of various polymer compositions when clays are present, there is a desire to have a nanocomposite with low air permeability.

Nanocomposites have been formed using brominated copolymers of isobutylene and *p*-methylstyrene. See, for example, *Elspass et al.*, US 5,807,629, 5,883,173, and 6,034,164. Further improvement in the uncured and cured properties of these elastomeric compositions can be achieved by the use of processing aids. Resins and oils (or "processing aids") such as naphthenic, paraffinic, and aliphatic resins may be used to improve the processability of elastomeric compounds. However, increased processability in the presence of oils and resins comes at the price of a loss of air impermeability and an increase in undesirable color, among other undesirable effects of various other properties.

Polybutene and paraffinic-type processing oils have been disclosed in US 4,279,284 to *Spadone*, US 5,964,969 to *Sandstrom et al.* and EP 0 314 416 to *Mohammed*. A paraffinic-type processing oil is disclosed in US 5,631,316 to *Costemalle et al.* Also, WO 94/01295 to *Gursky et al.* discloses the use of petroleum waxes and naphthenic oils and resins in a rubber composition for tire sidewalls, and U.S.S.N. 09/691,764, filed October 18, 2000 (assigned to the assignee of the present invention) to *Waddell et al.* discloses colorable rubber compositions. Other disclosures of processing oil or resin-containing elastomeric or adhesive compositions include US 5,005,625, 5,013,793, 5,162,409, 5,178,702, 5,234,987, 5,234,987, 5,242,727, 5,397,832, 5,733,621, 5,755,899, EP 0 682 071 A1, EP 0376 558B1, WO 92/16587, and JP11005874, JP05179068A and JO3028244. None of these disclosures solves the problem of improving

processability of elastomeric compositions useful for tires, air barriers, etc, while maintaining or improving the air impermeability of those compositions.

Thus, there is still a problem of achieving a nanocomposite suitable for an air barrier, in particular, an air barrier incorporating the copolymer (or "terpolymer") of a C₄ to C₇ isomonoolefin and a *p*-methylstyrene and a *p*-halomethylstyrene, and/or a halogenated branched-butyl rubber. While enhancing the barrier properties of elastomeric compositions, nanocomposite formation tends to be at the expense of processability.

Also, it remains problematic to incorporate natural rubber into blends with these copolymers, as some desirable properties are lost upon addition of the natural rubber. What is needed is an elastomeric composition and nanocomposite composition that maintains desirable air barrier qualities, but has improved processability that processing oils and resins may provide, even in the presence of natural rubber blends.

SUMMARY OF THE INVENTION

Embodiments of the present invention include an elastomeric composition comprising at least one random copolymer comprising a C₄ to C₇ isomonoolefin derived unit, at least one filler, and polybutene oil having a number average molecular weight greater than 400, and a viscosity of greater than 35 cSt at 100°C. The copolymer is selected from poly(isobutylene-*co-p*-methylstyrene), halogenated poly(isobutylene-*co-p*-methylstyrene), halogenated star-branched butyl rubber, halogenated butyl rubber, and mixtures thereof. The composition may also include a thermoplastic resin, a filler, and/or an exfoliating clay. Suitable thermoplastic resins include polyolefins, nylons, and other polymers. The filler is selected from calcium carbonate, clay, mica, silica and silicates, talc, titanium dioxide, starch and other organic fillers such as wood flower, and carbon black, and mixtures thereof. The exfoliated clay is selected from exfoliated

natural or synthetic montmorillonite, nontronite, beidellite, volkonskoite, laponite, hectorite, saponite, sauconite, magadite, kenyaite, stevensite, vermiculite, halloysite, aluminate oxides, hydrotalcite, and mixtures thereof. These compositions are useful in air barrier applications such as, for example, innerliners
5 for a tires.

DETAILED DESCRIPTION OF THE INVENTION

The term "phr" is parts per hundred rubber, and is a measure common in the art wherein components of a composition are measured relative to a major
10 elastomer component, based upon 100 parts by weight of the elastomer or elastomers.

As used herein, in reference to Periodic Table "Groups", the new numbering scheme for the Periodic Table Groups are used as in HAWLEY'S
15 CONDENSED CHEMICAL DICTIONARY 852 (13th ed. 1997).

The term "elastomer", as used herein, refers to any polymer or composition of polymers consistent with the ASTM D1566 definition. The term "elastomer" may be used interchangeably with the term "rubber", as used herein.
20

Elastomer

Compositions of the present invention include at least one elastomer. The elastomer in one embodiment of the invention is an isobutylene-based homopolymer or copolymer. These polymers can be described as random
25 copolymer of a C₄ to C₇ isomonoolefin derived unit, such as isobutylene derived unit, and at least one other polymerizable unit. The isobutylene-based copolymer may or may not be halogenated.

In one embodiment of the invention, the isobutylene-based elastomer is a
30 butyl-type rubber or branched butyl-type rubber, especially halogenated versions

of these elastomers. Useful elastomers are unsaturated butyl rubbers such as homopolymers and copolymers of olefins or isoolefins and multiolefins, or homopolymers of multiolefins. These and other types of elastomers suitable for the invention are well known and are described in RUBBER TECHNOLOGY 209-581 (Maurice Morton ed., Chapman & Hall 1995), THE VANDERBILT RUBBER HANDBOOK 105-122 (Robert F. Ohm ed., R.T. Vanderbilt Co., Inc. 1990), and *Edward Kresge and H.C. Wang* in 8 KIRK-OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY 934-955 (John Wiley & Sons, Inc. 4th ed. 1993). Non-limiting examples of unsaturated elastomers useful in the method and composition of the present invention are poly(isobutylene-co-isoprene), polyisoprene, polybutadiene, polyisobutylene, poly(styrene-co-butadiene), natural rubber, star-branched butyl rubber, and mixtures thereof. Useful elastomers in the present invention can be made by any suitable means known in the art, and the invention is not herein limited by the method of producing the elastomer.

Butyl rubbers are prepared by reacting a mixture of monomers, the mixture having at least (1) a C₄ to C₁₂ isoolefin monomer component such as isobutylene with (2) a multiolefin, monomer component. The isoolefin is in a range from 70 to 99.5 wt% by weight of the total monomer mixture in one embodiment, and 85 to 99.5 wt% in another embodiment. The multiolefin component is present in the monomer mixture from 30 to 0.5 wt% in one embodiment, and from 15 to 0.5 wt% in another embodiment. In yet another embodiment, from 8 to 0.5 wt% of the monomer mixture is multiolefin.

The isoolefin is a C₄ to C₁₂ compound, non-limiting examples of which are compounds such as isobutylene, isobutene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, 1-butene, 2-butene, methyl vinyl ether, indene, vinyltrimethylsilane, hexene, and 4-methyl-1-pentene. The multiolefin is a C₄ to C₁₄ multiolefin such as isoprene, butadiene, 2,3-dimethyl-1,3-butadiene, myrcene, 6,6-dimethyl-fulvene, hexadiene, cyclopentadiene, and piperylene, and other

monomers such as disclosed in EP 0 279 456 and US 5,506,316 and 5,162,425. Other polymerizable monomers such as styrene and dichlorostyrene are also suitable for homopolymerization or copolymerization in butyl rubbers. One embodiment of the butyl rubber polymer of the invention is obtained by reacting
5 95 to 99.5 wt% of isobutylene with 0.5 to 8 wt% isoprene, or from 0.5 wt% to 5.0 wt% isoprene in yet another embodiment. Butyl rubbers and methods of their production are described in detail in, for example, US 2,356,128, 3,968,076, 4,474,924, 4,068,051 and 5,532,312.

10 A commercial example of a desirable butyl rubber is EXXON™ BUTYL Grades of poly(isobutylene-co-isoprene), having a Mooney viscosity of from 32 ± 2 to 51 ± 5 (ML 1 + 8 at 125°C). Another commercial example of a desirable butyl-type rubber is VISTANEX™ polyisobutylene rubber having a molecular weight viscosity average of from 0.9 ± 0.15 to $2.11 \pm 0.23 \times 10^6$.

15 Another embodiment of the butyl rubber useful in the invention is a branched or "star-branched" butyl rubber. These rubbers are described in, for example, EP 0 678 529 B1, US 5,182,333 and 5,071,913. In one embodiment, the star-branched butyl rubber ("SBB") is a composition of a butyl rubber, either
20 halogenated or not, and a polydiene or block copolymer, either halogenated or not. The invention is not limited by the method of forming the SBB. The polydienes/block copolymer, or branching agents (hereinafter "polydienes"), are typically cationically reactive and are present during the polymerization of the butyl or halogenated butyl rubber, or can be blended with the butyl rubber to form
25 the SBB. The branching agent or polydiene can be any suitable branching agent, and the invention is not limited to the type of polydiene used to make the SBB.

In one embodiment, the SBB is typically a composition of the butyl or halogenated butyl rubber as described above and a copolymer of a polydiene and a
30 partially hydrogenated polydiene selected from the group including styrene,

polybutadiene, polyisoprene, polypiperylene, natural rubber, styrene-butadiene rubber, ethylene-propylene diene rubber (EPDM), ethylene-propylene rubber (EPM), styrene-butadiene-styrene and styrene-isoprene-styrene block copolymers. These polydienes are present, based on the monomer wt%, greater than 0.3 wt% in one embodiment, and from 0.3 to 3 wt% in another embodiment, and from 0.4 to 2.7 wt% in yet another embodiment.

A commercial embodiment of the SBB of the present invention is SB Butyl 4266 (ExxonMobil Chemical Company, Houston TX), having a Mooney viscosity (ML 1+8 at 125°C, ASTM D 1646) of from 34 to 44. Further, cure characteristics of SB Butyl 4266 are as follows: MH is 69 ± 6 dN·m, ML is 11.5 ± 4.5 dN·m (ASTM D2084).

The isobutylene-based rubber may also be halogenated in a desirable embodiment of the isobutylene-based copolymer useful in the invention. Halogenated butyl rubber is produced by the halogenation of the butyl rubber product described above. Halogenation can be carried out by any means, and the invention is not herein limited by the halogenation process. Methods of halogenating polymers such as butyl polymers are disclosed in US 2,631,984, 3,099,644, 4,554,326, 4,681,921, 4,650,831, 4,384,072, 4,513,116 and 5,681,901. In one embodiment, the butyl rubber is halogenated in hexane diluent at from 4 to 60°C using bromine (Br₂) or chlorine (Cl₂) as the halogenation agent. The halogenated butyl rubber has a Mooney Viscosity of from 20 to 70 (ML 1+8 at 125°C) in one embodiment, and from 25 to 55 in another embodiment. The halogen wt% is from 0.1 to 10 wt% based in on the weight of the halogenated butyl rubber in one embodiment, and from 0.5 to 5 wt% in another embodiment. In yet another embodiment, the halogen wt% of the halogenated butyl rubber is from 1 to 2.5 wt%.

A commercial embodiment of the halogenated butyl rubber of the present invention is Bromobutyl 2222 (ExxonMobil Chemical Company). Its Mooney Viscosity is from 27 to 37 (ML 1+8 at 125°C, ASTM 1646, modified), and the bromine content is from 1.8 to 2.2 wt% relative to the Bromobutyl 2222. Further, cure characteristics of Bromobutyl 2222 are as follows: MH is from 28 to 40 dN·m, ML is from 7 to 18 dN·m (ASTM D2084). Another commercial embodiment of the halogenated butyl rubber is Bromobutyl 2255 (ExxonMobil Chemical Company). Its Mooney Viscosity is from 41 to 51 (ML 1+8 at 125°C, ASTM D1646), and the bromine content is from 1.8 to 2.2 wt%. Further, cure characteristics of Bromobutyl 2255 are as follows: MH is from 34 to 48 dN·m, ML is from 11 to 21 dN·m (ASTM D2084).

In another embodiment of the brominated rubber component of the invention, a branched or "star-branched" halogenated butyl rubber is used. In one embodiment, the halogenated star-branched butyl rubber ("HSSB") is a composition of a butyl rubber, either halogenated or not, and a polydiene or block copolymer, either halogenated or not. The halogenation process is described in detail in US 4,074,035, 5,071,913, 5,286,804, 5,182,333 and 6,228,978. The invention is not limited by the method of forming the HSSB. The polydienes/block copolymer, or branching agents (hereinafter "polydienes"), are typically cationically reactive and are present during the polymerization of the butyl or halogenated butyl rubber, or can be blended with the butyl or halogenated butyl rubber to form the HSSB. The branching agent or polydiene can be any suitable branching agent, and the invention is not limited to the type of polydiene used to make the HSSB.

In one embodiment, the HSSB is typically a composition of the butyl or halogenated butyl rubber as described above and a copolymer of a polydiene and a partially hydrogenated polydiene selected from the group including styrene, polybutadiene, polyisoprene, polypiperylene, natural rubber, styrene-butadiene

rubber, ethylene-propylene diene rubber, styrene-butadiene-styrene and styrene-isoprene-styrene block copolymers. These polydienes are present, based on the monomer wt%, greater than 0.3 wt% in one embodiment, and from 0.3 to 3 wt% in another embodiment, and from 0.4 to 2.7 wt% in yet another embodiment.

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A commercial embodiment of the HSSB of the present invention is Bromobutyl 6222 (ExxonMobil Chemical Company), having a Mooney Viscosity (ML 1+8 at 125°C, ASTM D1646) of from 27 to 37, and a bromine content of from 2.2 to 2.6 wt% relative to the HSSB. Further, cure characteristics of
10 Bromobutyl 6222 are as follows: MH is from 24 to 38 dN·m, ML is from 6 to 16 dN·m (ASTM D2084).

Another embodiment of the isobutylene-based elastomer useful in the invention is an isoolefin copolymer comprising a halomethylstyrene derived unit.
15 The elastomer in one embodiment of the invention is a random copolymer of comprising at least C₄ to C₇ isoolefin derived units, such as isobutylene derived units, and halomethylstyrene derived units. The halomethylstyrene unit may be an ortho-, meta-, or para-alkyl-substituted styrene unit. In one embodiment, the halomethylstyrene derived unit is a *p*-halomethylstyrene containing at least 80%,
20 more preferably at least 90% by weight of the para-isomer. The "halo" group can be any halogen, desirably chlorine or bromine. The halogenated elastomer may also include functionalized interpolymers wherein at least some of the alkyl substituents groups present in the styrene monomer units contain benzylic halogen or some other functional group described further below. These interpolymers are
25 herein referred to as "isoolefin copolymers comprising a halomethylstyrene derived unit" or simply "isoolefin copolymer".

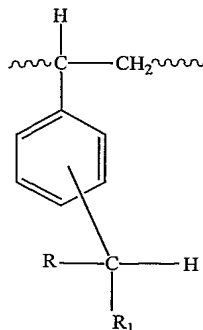
The isoolefin copolymer may also include other monomer derived units. The isoolefin of the copolymer may be a C₄ to C₁₂ compound, non-limiting
30 examples of which are compounds such as isobutylene, isobutene, 2-methyl-1-

butene, 3-methyl-1-butene, 2-methyl-2-butene, 1-butene, 2-butene, methyl vinyl ether, indene, vinyltrimethylsilane, hexene, and 4-methyl-1-pentene. The copolymer may also further comprise multiolefin derived units. The multiolefin is a C₄ to C₁₄ multiolefin such as isoprene, butadiene, 2,3-dimethyl-1,3-butadiene, myrcene, 6,6-dimethyl-fulvene, hexadiene, cyclopentadiene, and piperylene, and other monomers such as disclosed in EP 0 279 456 and US 5,506,316 and 5,162,425. Desirable styrenic monomer derived units that may comprise the copolymer include styrene, methylstyrene, chlorostyrene, methoxystyrene, indene and indene derivatives, and combinations thereof.

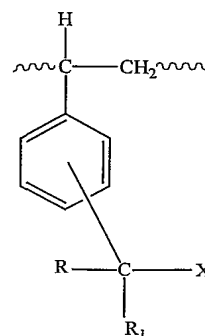
In another embodiment of the invention, the interpolymer is a random elastomeric copolymer of an ethylene derived unit or a C₃ to C₆ α-olefin derived unit and an halomethylstyrene derived unit, preferably *p*-halomethylstyrene containing at least 80%, more preferably at least 90% by weight of the para-isomer and also include functionalized interpolymers wherein at least some of the alkyl substituents groups present in the styrene monomer units contain benzylic halogen or some other functional group.

Preferred isoolefin copolymers may be characterized as interpolymers containing the following monomer units randomly spaced along the polymer chain:

1.



2.



wherein R and R¹ are independently hydrogen, lower alkyl, preferably C₁ to C₇ alkyl and primary or secondary alkyl halides and X is a functional group such as halogen. Desirable halogens are chlorine, bromine or combinations thereof. Preferably R and R¹ are each hydrogen. The -CRR₁H and -CRR₁X groups can be substituted on the styrene ring in either the ortho, meta, or para positions, preferably para. Up to 60 mole % of the *p*-substituted styrene present in the interpolymer structure may be the functionalized structure (2) above in one embodiment, and in another embodiment from 0.1 to 5 mol%. In yet another embodiment, the amount of functionalized structure (2) is from 0.4 to 1 mol%.

The functional group X may be halogen or some other functional group which may be incorporated by nucleophilic substitution of benzylic halogen with other groups such as carboxylic acids; carboxy salts; carboxy esters, amides and imides; hydroxy; alkoxide; phenoxide; thiolate; thioether; xanthate; cyanide; cyanate; amino and mixtures thereof. These functionalized isomonoolefin copolymers, their method of preparation, methods of functionalization, and cure are more particularly disclosed in US 5,162,445.

Most useful of such functionalized materials are elastomeric random interpolymers of isobutylene and *p*-methylstyrene containing from 0.5 to 20 mole % *p*-methylstyrene wherein up to 60 mole% of the methyl substituent groups present on the benzyl ring contain a bromine or chlorine atom, preferably a bromine atom (*p*-bromomethylstyrene), as well as acid or ester functionalized versions thereof wherein the halogen atom has been displaced by maleic anhydride or by acrylic or methacrylic acid functionality. These interpolymers are termed "halogenated poly(isobutylene-*co-p*-methylstyrene)" or "brominated poly(isobutylene-*co-p*-methylstyrene)", and are commercially available under the name EXXPRO™ Elastomers (ExxonMobil Chemical Company, Houston TX). It is understood that the use of the terms "halogenated" or "brominated" are not limited to the method of halogenation of the copolymer, but merely descriptive of

the copolymer which comprises the isobutylene derived units, the *p*-methylstyrene derived units, and the *p*-halomethylstyrene derived units.

These functionalized polymers preferably have a substantially
5 homogeneous compositional distribution such that at least 95% by weight of the polymer has a *p*-alkylstyrene content within 10% of the average *p*-alkylstyrene content of the polymer. More preferred polymers are also characterized by a narrow molecular weight distribution (M_w/M_n) of less than 5, more preferably less than 2.5, a preferred viscosity average molecular weight in the range of from
10 200,000 up to 2,000,000 and a preferred number average molecular weight in the range of from 25,000 to 750,000 as determined by gel permeation chromatography.

The copolymers may be prepared by a slurry polymerization of the
15 monomer mixture using a Lewis acid catalyst, followed by halogenation, preferably bromination, in solution in the presence of halogen and a radical initiator such as heat and/or light and/or a chemical initiator and, optionally, followed by electrophilic substitution of bromine with a different functional derived unit.

20 Preferred halogenated poly(isobutylene-*co-p*-methylstyrene) are brominated polymers which generally contain from 0.1 to 5 wt% of bromomethyl groups. In yet another embodiment, the amount of bromomethyl groups is from 0.2 to 2.5 wt%. Expressed another way, preferred copolymers contain from 0.05
25 up to 2.5 mole% of bromine, based on the weight of the polymer, more preferably from 0.1 to 1.25 mole % bromine, and are substantially free of ring halogen or halogen in the polymer backbone chain. In one embodiment of the invention, the interpolymer is a copolymer of C_4 to C_7 isomonoolefin derived units, a *p*-methylstyrene derived units and a *p*-halomethylstyrene derived units, wherein the
30 *p*-halomethylstyrene units are present in the interpolymer from 0.4 to 1 mol%

based on the interpolmer. In another embodiment, the *p*-halomethylstyrene is *p*-bromomethylstyrene. The Mooney Viscosity (1+8, 125°C, ASTM D1646, modified) is from 30 to 60 MU.

5 The elastomeric component present in compositions of the invention may contain various amounts of one, two, or more different elastomers. For example, embodiments of compositions of the invention may contain from 5 to 100 phr of halogenated butyl rubber, from 5 to 95 phr of star-branched butyl rubber, from 5 to 95 phr of halogenated star-branched butyl rubber, or from 5 to 95 phr of
10 halogenated poly(isobutylene-*co-p*-methylstyrene). In another embodiment, the compositions contain from 40 to 100 phr of halogenated poly(isobutylene-*co-p*-methylstyrene), and/or from 40 to 100 phr of halogenated star-branched butyl rubber (HSSB). The elastomeric compositions of the invention may contain other elastomers, or so called "secondary" elastomer components.

15

Secondary Elastomeric Component

 A secondary elastomeric component may be present in compositions of the present invention. These rubbers include, but are not limited to, natural rubbers, polyisoprene rubber, styrene butadiene rubber (SBR), polybutadiene rubber,
20 isoprene butadiene rubber (IBR), styrene-isoprene-butadiene rubber (SIBR), ethylene-propylene rubber, ethylene-propylene-diene rubber (EPDM), polysulfide, nitrile rubber, propylene oxide polymers, star-branched butyl rubber and halogenated star-branched butyl rubber, brominated butyl rubber, chlorinated butyl rubber, star-branched polyisobutylene rubber, star-branched brominated butyl (polyisobutylene/isoprene copolymer) rubber; isobutylene/methylstyrene
25 copolymers such as isobutylene/meta-bromomethylstyrene, isobutylene/bromomethylstyrene, isobutylene/chloromethylstyrene, halogenated isobutylene cyclopentadiene, and isobutylene/chloromethylstyrene and mixtures thereof.

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A secondary rubber component may also be present in the composition and air barrier of the invention. An embodiment of the secondary rubber component present is natural rubber. Natural rubbers are described in detail by *Subramaniam* in RUBBER TECHNOLOGY 179-208 (1995). Desirable embodiments of the natural
5 rubbers of the present invention are selected from the group consisting of Malaysian rubber such as SMR CV, SMR 5, SMR 10, SMR 20, and SMR 50 and mixtures thereof, wherein the natural rubbers have a Mooney viscosity at 100°C (ML 1+4) of from 30 to 120, more preferably from 40 to 65. The Mooney viscosity test referred to herein is in accordance with ASTM D-1646.

10

Some commercial examples of synthetic secondary rubbers useful in the present invention are NATSYN™ (Goodyear Chemical Company), and BUDENE™ 1207 or BR 1207 (Goodyear Chemical Company). A desirable rubber is high cis-polybutadiene (cis-BR). By "cis-polybutadiene" or "high cis-
15 polybutadiene", it is meant that 1,4-cis polybutadiene is used, wherein the amount of cis component is at least 95%. An example of high cis-polybutadiene commercial products used in the composition BUDENE™ 1207. A suitable ethylene-propylene rubber is commercially available as VISTALON™ (ExxonMobil Chemical Company).

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In one embodiment of the invention, a so called semi-crystalline copolymer (SCC) is present as the secondary rubber. Semi-crystalline copolymers are described in U.S.S.N. 09/569,363, filed on May 11, 2000 (assigned to the assignee of the present invention). Generally, the SCC is a copolymer of ethylene
25 or propylene derived units and α -olefin derived units, the α -olefin having from 4 to 16 carbon atoms in one embodiment, and in another embodiment the SCC is a copolymer of ethylene derived units and α -olefin derived units, the α -olefin having from 4 to 10 carbon atoms, wherein the SCC has some degree of crystallinity. In a further embodiment, the SCC is a copolymer of 1-butene derived units and
30 another α -olefin derived unit, the other α -olefin having from 5 to 16 carbon atoms,

wherein the SCC also has some degree of crystallinity. The SCC can also be a copolymer of ethylene and styrene.

The secondary rubber component of the elastomer composition may be present in a range from up to 50 phr in one embodiment, from up to 40 phr in another embodiment, and from up to 30 phr in yet another embodiment.

Thermoplastic resin

The compositions of the invention may optionally include a thermoplastic resin. Thermoplastic resins suitable for practice of the present invention may be used singly or in combination and are resins containing nitrogen, oxygen, halogen, sulfur or other groups capable of interacting with an aromatic functional groups such as halogen or acidic groups. The resins are present in the nanocomposite from 30 to 90 wt% of the nanocomposite in one embodiment, and from 40 to 80 wt% in another embodiment, and from 50 to 70 wt% in yet another embodiment. In yet another embodiment, the resin is present at a level of greater than 40 wt% of the nanocomposite, and greater than 60 wt% in another embodiment.

Suitable thermoplastic resins include resins selected from the group consisting of polyamides, polyimides, polycarbonates, polyesters, polysulfones, polylactones, polyacetals, acrylonitrile-butadiene-styrene resins (ABS), polyphenyleneoxide (PPO), polyphenylene sulfide (PPS), polystyrene, styrene-acrylonitrile resins (SAN), styrene maleic anhydride resins (SMA), aromatic polyketones (PEEK, PED, and PEKK) and mixtures thereof.

Suitable thermoplastic polyamides (nylons) comprise crystalline or resinous, high molecular weight solid polymers including copolymers and terpolymers having recurring amide units within the polymer chain. Polyamides may be prepared by polymerization of one or more epsilon lactams such as caprolactam, pyrrolidione, lauryllactam and aminoundecanoic lactam, or amino

acid, or by condensation of dibasic acids and diamines. Both fiber-forming and molding grade nylons are suitable. Examples of such polyamides are polycaprolactam (nylon-6), polylauryllactam (nylon-12), polyhexamethyleneadipamide (nylon-6,6) polyhexamethyleneazelaamide (nylon-6,9), polyhexamethylenesebacamide (nylon-6,10), polyhexamethyleneisophthalamide (nylon-6, IP) and the condensation product of 11-amino-undecanoic acid (nylon-11). Additional examples of satisfactory polyamides (especially those having a softening point below 275°C) are described in 16 ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY 1-105 (John Wiley & Sons 1968), CONCISE ENCYCLOPEDIA OF POLYMER SCIENCE AND 748-761 (John Wiley & Sons, 1990), and 10 ENCYCLOPEDIA OF POLYMER SCIENCE AND TECHNOLOGY 392-414 (John Wiley & Sons 1969). Commercially available thermoplastic polyamides may be advantageously used in the practice of this invention, with linear crystalline polyamides having a softening point or melting point between 160 and 260°C being preferred.

Suitable thermoplastic polyesters which may be employed include the polymer reaction products of one or a mixture of aliphatic or aromatic polycarboxylic acids esters of anhydrides and one or a mixture of diols. Examples of satisfactory polyesters include poly (trans-1,4-cyclohexylene C₂₋₆ alkane dicarboxylates such as poly(trans-1,4-cyclohexylene succinate) and poly (trans-1,4-cyclohexylene adipate); poly (cis or trans-1,4-cyclohexanedimethylene) alkanedicarboxylates such as poly(cis-1,4-cyclohexanedimethylene) oxlate and poly-(cis-1,4-cyclohexanedimethylene) succinate, poly (C₂₋₄ alkylene terephthalates) such as polyethyleneterephthalate and polytetramethylene-terephthalate, poly (C₂₋₄ alkylene isophthalates such as polyethyleneisophthalate and polytetramethylene-isophthalate and like materials. Preferred polyesters are derived from aromatic dicarboxylic acids such as naphthalenic or phthalic acids and C₂ to C₄ diols, such as polyethylene terephthalate and polybutylene

terephthalate. Preferred polyesters will have a melting point in the range of 160°C to 260°C.

Poly(phenylene ether) (PPE) thermoplastic resins which may be used in accordance with this invention are well known, commercially available materials produced by the oxidative coupling polymerization of alkyl substituted phenols. They are generally linear, amorphous polymers having a glass transition temperature in the range of 190°C to 235°C. These polymers, their method of preparation and compositions with polystyrene are further described in US 3,383,435.

Other thermoplastic resins which may be used include the polycarbonate analogs of the polyesters described above such as segmented poly (ether *co*-phthalates); polycaprolactone polymers; styrene resins such as copolymers of styrene with less than 50 mol% of acrylonitrile (SAN) and resinous copolymers of styrene, acrylonitrile and butadiene (ABS); sulfone polymers such as polyphenyl sulfone; copolymers and homopolymers of ethylene and C₂ to C₈ α -olefins, in one embodiment a homopolymer of propylene derived units, and in another embodiment a random copolymer or block copolymer of ethylene derived units and propylene derived units, and like thermoplastic resins as are known in the art.

Polybutene processing oil

Polybutene processing oil is present in the composition of the invention. In one embodiment of the invention, the polybutene processing oil is a low molecular weight (less than 15,000 Mn) homopolymer or copolymer of olefin derived units having from 3 to 8 carbon atoms in one embodiment, preferably from 4 to 6 carbon atoms in another embodiment. In yet another embodiment, the polybutene is a homopolymer or copolymer of a C₄ raffinate. An embodiment of such low molecular weight polymers termed "polybutene" polymers is described in, for example, SYNTHETIC LUBRICANTS AND HIGH-PERFORMANCE FUNCTIONAL

FLUIDS 357-392 (Leslie R. Rudnick & Ronald L. Shubkin, ed., Marcel Dekker 1999) (hereinafter "polybutene processing oil" or "polybutene").

In one embodiment of the invention, the polybutene processing oil is a
5 copolymer of at least isobutylene derived units, 1-butene derived units, and 2-
butene derived units. In one embodiment, the polybutene is a homopolymer,
copolymer, or terpolymer of the three units, wherein the isobutylene derived units
are from 40 to 100 wt% of the copolymer, the 1-butene derived units are from 0 to
40 wt% of the copolymer, and the 2-butene derived units are from 0 to 40 wt% of
10 the copolymer. In another embodiment, the polybutene is a copolymer or
terpolymer of the three units, wherein the isobutylene derived units are from 40 to
99 wt% of the copolymer, the 1-butene derived units are from 2 to 40 wt% of the
copolymer, and the 2-butene derived units are from 0 to 30 wt% of the copolymer.
In yet another embodiment, the polybutene is a terpolymer of the three units,
15 wherein the isobutylene derived units are from 40 to 96 wt% of the copolymer, the
1-butene derived units are from 2 to 40 wt% of the copolymer, and the 2-butene
derived units are from 2 to 20 wt% of the copolymer. In yet another embodiment,
the polybutene is a homopolymer or copolymer of isobutylene and 1-butene,
wherein the isobutylene derived units are from 65 to 100 wt% of the
20 homopolymer or copolymer, and the 1-butene derived units are from 0 to 35 wt%
of the copolymer.

Polybutene processing oils useful in the invention typically have a number
average molecular weight (M_n) of less than 10,000 in one embodiment, less than
25 8000 in another embodiment, and less than 6000 in yet another embodiment. In
one embodiment, the polybutene oil has a number average molecular weight of
greater than 400, and greater than 700 in another embodiment, and greater than
900 in yet another embodiment. A preferred embodiment can be a combination of
any lower limit with any upper limit herein. For example, in one embodiment of
30 the polybutene of the invention, the polybutene has a number average molecular

weight of from 400 to 10,000, and from 700 to 8000 in another embodiment. Useful viscosities of the polybutene processing oil ranges from 10 to 6000 cSt (centiStokes) at 100°C in one embodiment, and from 35 to 5000 cSt at 100°C in another embodiment, and is greater than 35 cSt at 100°C in yet another
5 embodiment, and greater than 100 cSt at 100°C in yet another embodiment.

Commercial examples of such a processing oil are the PARAPOL™ Series of processing oils (ExxonMobil Chemical Company, Houston TX), such as PARAPOL™ 450, 700, 950, 1300, 2400 and 2500. The commercially available
10 PARAPOL™ Series of polybutene processing oils are synthetic liquid polybutenes, each individual formulation having a certain molecular weight, all formulations of which can be used in the composition of the invention. The molecular weights of the PARAPOL™ oils are from 420 Mn (PARAPOL™ 450) to 2700 Mn (PARAPOL™ 2500) as determined by gel permeation
15 chromatography. The MWD of the PARAPOL™ oils range from 1.8 to 3 in one embodiment, and from 2 to 2.8 in another embodiment.

Below, Table 1 shows some of the properties of the PARAPOL™ oils useful in embodiments of the present invention, wherein the viscosity was
20 determined as per ASTM D445-97, and the molecular weight by gel permeation chromatography.

Table 1. Properties of individual PARAPOL™ Grades

Grade	Mn	Viscosity @ 100°C, cSt
450	420	10.6
700	700	78
950	950	230
1300	1300	630
2400	2350	3200
2500	2700	4400

5 Other properties of PARAPOL™ processing oils are as follows: the density (g/mL) of PARAPOL™ processing oils varies from about 0.85 (PARAPOL™ 450) to 0.91 (PARAPOL™ 2500). The bromine number (CG/G) for PARAPOL™ oils ranges from 40 for the 450 Mn processing oil, to 8 for the 2700 Mn processing oil.

10 The elastomeric composition of the invention may include one or more types of polybutene as a mixture, blended either prior to addition to the elastomer, or with the elastomer. The amount and identity (*e.g.*, viscosity, Mn, etc.) of the polybutene processing oil mixture can be varied in this manner. Thus, PARAPOL™ 450 can be used when low viscosity is desired in the composition of the invention, while PARAPOL™ 2500 can be used when a higher viscosity is desired, or compositions thereof to achieve some other viscosity or molecular weight. In this manner, the physical properties of the composition can be controlled. More particularly, the phrases "polybutene processing oil", or 15 "polybutene processing oil" include a single oil or a composition of two or more oils used to obtain any viscosity or molecular weight (or other property) desired, as specified in the ranges disclosed herein.

The polybutene processing oil or oils are present in the elastomeric composition of the invention from 1 to 60 phr in one embodiment, and from 2 to 40 phr in another embodiment, from 4 to 35 phr in another embodiment, and from 5 to 30 phr in yet another embodiment. Preferably, the polybutene processing oil
5 does not contain aromatic groups or unsaturation.

Filler and Clay

The elastomeric composition may have one or more filler components such as calcium carbonate, clay, mica, silica and silicates, talc, titanium dioxide, starch
10 and other organic fillers such as wood flower, and carbon black. In one embodiment, the filler is carbon black or modified carbon black. The preferred filler is semi-reinforcing grade carbon black present at a level of from 10 to 150 phr of the composition, more preferably from 30 to 120 phr. Useful grades of carbon black as described in RUBBER TECHNOLOGY 59-85 (1995) range from
15 N110 to N990. More desirably, embodiments of the carbon black useful in, for example, tire treads are N229, N351, N339, N220, N234 and N110 provided in ASTM (D3037, D1510, and D3765). Embodiments of the carbon black useful in, for example, sidewalls in tires, are N330, N351, N550, N650, N660, and N762. Embodiments of the carbon black useful in, for example, innerliners or innertubes
20 are N550, N650, N660, N762, N990, and Regal 85 (Cabot Corporation Alpharetta, GA) and the like.

Exfoliated clays may also be present in the composition. These clays, also referred to as "nanoclays", are well known, and their identity, methods of
25 preparation and blending with polymers is disclosed in, for example, JP 2000109635, 2000109605, 11310643; DE 19726278; WO98/53000; US 5,091,462, 4,431,755, 4,472,538, and 5,910,523. Swellable layered clay materials suitable for the purposes of this invention include natural or synthetic phyllosilicates, particularly smectic clays such as montmorillonite, nontronite,
30 beidellite, volkonskoite, laponite, hectorite, saponite, sauconite, magadite,

kenyaite, stevensite and the like, as well as vermiculite, halloysite, aluminate oxides, hydrotalcite and the like. These layered clays generally comprise particles containing a plurality of silicate platelets having a thickness of from 4-20Å in one embodiment, 8-12Å in another embodiment, bound together and contain
5 exchangeable cations such as Na^+ , Ca^{+2} , K^+ or Mg^{+2} present at the interlayer surfaces.

The layered clay may be intercalated and exfoliated by treatment with organic molecules (swelling agents) capable of undergoing ion exchange reactions
10 with the cations present at the interlayer surfaces of the layered silicate. Suitable swelling agents include cationic surfactants such as ammonium, alkylamines or alkylammonium (primary, secondary, tertiary and quaternary), phosphonium or sulfonium derivatives of aliphatic, aromatic or arylaliphatic amines, phosphines and sulfides. Desirable amine compounds (or the corresponding ammonium ion)
15 are those with the structure $\text{R}_1\text{R}_2\text{R}_3\text{N}$, wherein R_1 , R_2 , and R_3 are C_1 to C_{20} alkyls or alkenes which may be the same or different. In one embodiment, the exfoliating agent is a so called long chain tertiary amine, wherein at least R_1 is a C_{14} to C_{20} alkyl or alkene.

20 Another class of swelling agents include those which can be covalently bonded to the interlayer surfaces. These include polysilanes of the structure - $\text{Si}(\text{R}')_2\text{R}^2$ where R' is the same or different at each occurrence and is selected from alkyl, alkoxy or oxysilane and R^2 is an organic radical compatible with the matrix polymer of the composite.

25 Other suitable swelling agents include protonated amino acids and salts thereof containing 2-30 carbon atoms such as 12-aminododecanoic acid, epsilon-caprolactam and like materials. Suitable swelling agents and processes for intercalating layered silicates are disclosed in US 4,472,538, 4,810,734, 4,889,885
30 as well as WO92/02582.

In a preferred embodiment of the invention, the exfoliating additive is combined with a halogenated polymer. In one embodiment, the additive includes all primary, secondary and tertiary amines and phosphines; alkyl and aryl sulfides and thiols; and their polyfunctional versions. Desirable additives include: long-chain tertiary amines such as N,N-dimethyl-octadecylamine, N,N-dioctadecyl-methylamine, so called dihydrogenated tallowalkyl-methylamine and the like, and amine-terminated polytetrahydrofuran; long-chain thiol and thiosulfate compounds like hexamethylene sodium thiosulfate. In another embodiment of the invention, improved interpolymer impermeability is achieved by the presence of polyfunctional curatives such as hexamethylene bis(sodium thiosulfate) and hexamethylene bis(cinnamaldehyde).

The amount of clay or exfoliated clay incorporated in the nanocomposites in accordance with this invention is sufficient to develop an improvement in the mechanical properties or barrier properties of the nanocomposite, e.g tensile strength or air/oxygen permeability. Amounts generally will range from 0.5 to 15 wt% in one embodiment, and from 1 to 10 wt% in another embodiment, and from 1 to 5 in yet another embodiment, based on the polymer content of the nanocomposite. Expressed in parts per hundred rubber, the clay or exfoliated clay may be present from 1 to 30 phr in one embodiment, and from 3 to 20 phr in another embodiment. In one embodiment, the exfoliated clay is an alkylamine-exfoliated clay.

Curing Agents and Accelerators

The compositions produced in accordance with the present invention typically contain other components and additives customarily used in rubber mixes, such as pigments, accelerators, cross-linking and curing materials, antioxidants, antiozonants, and fillers. In one embodiment, processing aids (resins) such as naphthenic, aromatic or paraffinic extender oils may be present from 1 to 30 phr. In

another embodiment, naphthenic, aliphatic, paraffinic and other aromatic resins and oils are substantially absent from the composition. By "substantially absent", it is meant that naphthenic, aliphatic, paraffinic and other aromatic resins are present, if at all, to an extent no greater than 2 phr in the composition.

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Generally, polymer compositions, e.g., those used to produce tires, are crosslinked. It is known that the physical properties, performance characteristics, and durability of vulcanized rubber compounds are directly related to the number (crosslink density) and type of crosslinks formed during the vulcanization reaction. (See, e.g., Helt et al., *The Post Vulcanization Stabilization for NR*, RUBBER WORLD 18-23 (1991). Cross-linking and curing agents include sulfur, zinc oxide, and fatty acids. Peroxide cure systems may also be used. Generally, polymer compositions may be crosslinked by adding curative molecules, for example sulfur, metal oxides (i.e., zinc oxide), organometallic compounds, radical initiators, etc. followed by heating. In particular, the following are common curatives that will function in the present invention: ZnO, CaO, MgO, Al₂O₃, CrO₃, FeO, Fe₂O₃, and NiO. These metal oxides can be used in conjunction with the corresponding metal stearate complex (e.g., Zn(Stearate)₂, Ca(Stearate)₂, Mg(Stearate)₂, and Al(Stearate)₃), or with stearic acid, and either a sulfur compound or an alkylperoxide compound. (See also, *Formulation Design and Curing Characteristics of NBR Mixes for Seals*, RUBBER WORLD 25-30 (1993). This method may be accelerated and is often used for the vulcanization of elastomer compositions.

Accelerators include amines, guanidines, thioureas, thiazoles, thiurams, sulfenamides, sulfenimides, thiocarbamates, xanthates, and the like. Acceleration of the cure process may be accomplished by adding to the composition an amount of the accelerant. The mechanism for accelerated vulcanization of natural rubber involves complex interactions between the curative, accelerator, activators and polymers. Ideally, all of the available curative is consumed in the formation of effective crosslinks which join together two polymer chains and enhance the overall

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strength of the polymer matrix. Numerous accelerators are known in the art and include, but are not limited to, the following: stearic acid, diphenyl guanidine (DPG), tetramethylthiuram disulfide (TMTD), 4,4'-dithiodimorpholine (DTDM), tetrabutylthiuram disulfide (TBTD), 2,2'-benzothiazyl disulfide (MBTS),
5 hexamethylene-1,6-bisthiosulfate disodium salt dihydrate, 2-(morpholiniothio) benzothiazole (MBS or MOR), compositions of 90% MOR and 10% MBTS (MOR 90), N-tertiarybutyl-2-benzothiazole sulfenamide (TBBS), and N-oxydiethylene thiocarbamyl-N-oxydiethylene sulfonamide (OTOS), zinc 2-ethyl hexanoate (ZEH), N, N'-diethyl thiourea.

10 In one embodiment of the invention, at least one curing agent is present from 0.2 to 15 phr, and from 0.5 to 10 phr in another embodiment. Curing agents include those components described above that facilitate or influence the cure of elastomers, such as metals, accelerators, sulfur, peroxides, and other agents common in the art,
15 and as described above.

Processing

Mixing of the components may be carried out by combining the polymer components and the clay in the form of an intercalate in any suitable mixing
20 device such as a Banbury™ mixer, Brabender™ mixer or preferably a mixer/extruder. Mixing is performed at temperatures in the range from up to the melting point of the elastomer and/or secondary rubber used in the composition in one embodiment, from 80° C up to 340° C in another embodiment, and from 120° C to 300° C in yet another embodiment, under conditions of shear sufficient to allow
25 the clay intercalate to exfoliate and become uniformly dispersed within the polymer to form the nanocomposite.

In the example compositions, the mixing was performed in a BR Banbury™ internal mixer by techniques known in the art. Typically, from 70% to
30 100% of the elastomer or elastomers is first mixed for 20 to 90 seconds, or until

the temperature reaches from 40 to 60°C. Then, 3/4 of the filler, and the remaining amount of elastomer, if any, is typically added to the mixer, and mixing continues until the temperature reaches from 90 to 150°C. Next, the remaining filler is added, as well as the processing oil, and mixing continues until the
5 temperature reaches from 140 to 190°C. The finished mixture is then finished by sheeting on an open mill and allowed to cool to from 60°C to 100°C when the curatives are added.

Mixing with the clays is performed by techniques known to those skilled
10 in the art, wherein the clay is added to the polymer at the same time as the carbon black in one embodiment. The polybutene processing oil is typically added later in the mixing cycle after the carbon black and clay have achieved adequate dispersion in the elastomeric matrix.

The cured compositions of the invention can include various elastomers
15 and fillers with the polybutene processing oil. The compositions of the invention typically include isobutylene-based elastomers such as halogenated poly(isobutylene-*co-p*-methylstyrene), butyl rubber, or halogenated star-branched butyl rubber (HSSB) either alone, or some combination with one another, with the
20 polybutene processing oil being present from 5 to 30 phr in one embodiment.

In one embodiment, the composition is halogenated poly(isobutylene-*co-p*-
methylstyrene) from 50 to 100 phr that may include natural rubber from 5 to 50
25 phr, and polybutene processing oil present from 5 to 30 phr, a filler such as a carbon black from 20 to 80 phr, and an exfoliating clay from 0.5 to 20 phr in one embodiment, and from 2 to 15 phr in another embodiment. The cure agents such as phenolic resins, sulfur, stearic acid, and zinc oxide, may be present from 0.1 to 5 phr.

In another embodiment, the composition may be a HSSB present from 50 to 100 phr that may include a halogenated poly(isobutylene-*co-p*-methylstyrene) from 5 to 95 phr in one embodiment, and from 20 to 70 phr in another embodiment, and polybutene processing oil present from 3 to 30 phr, a filler such as a carbon black from 20 to 80 phr, and an exfoliating clay from 0.5 to 20 phr in one embodiment, and from 2 to 15 phr in another embodiment. The cure agents such as phenolic resins, sulfur, stearic acid, and zinc oxide, may be present from 0.1 to 5 phr.

In yet another embodiment, the composition may be a halogenated butyl rubber present from 50 to 100 phr that may include a halogenated poly(isobutylene-*co-p*-methylstyrene) from 5 to 95 phr in one embodiment, and from 20 to 70 phr in another embodiment, and polybutene processing oil present from 3 to 30 phr, a filler such as a carbon black from 20 to 80 phr, and an exfoliating clay from 0.5 to 20 phr in one embodiment, and from 2 to 15 phr in another embodiment. The cure agents such as phenolic resins, sulfur, stearic acid, and zinc oxide, may be present from 0.1 to 5 phr.

The isobutylene-based elastomer useful in the invention can be blended with various other rubbers or plastics as disclosed herein, in particular thermoplastic resins such as nylons or polyolefins such as polypropylene or copolymers of polypropylene. These compositions are useful in air barriers such as bladders and innerliners, air sleeves (such as in air shocks), diaphragms, as well as other applications where high air or oxygen retention is desirable. In one embodiment, the cured composition has an air (air, oxygen or nitrogen at 65°C) permeability of from 1.2×10^{-8} to 4×10^{-8} cm³-cm/cm²-sec-atm, and from 1.5×10^{-8} to 3.5×10^{-8} cm³-cm/cm²-sec-atm in another embodiment.

In one embodiment, an air barrier can be made by the method of combining at least one random copolymer comprising a C₄ to C₇ isomonoolefin

derived unit, at least one filler, and polybutene oil having a number average molecular weight greater than 400, and at least one cure agent; and curing the combined components as described above.

5 **Test Methods**

Cure properties were measured using an ODR 2000 at the indicated temperature and 1 or 3 degree arc. Test specimens were cured at the indicated temperature, typically from 150°C to 160°C, for a time corresponding to T_{c90} + appropriate mold lag. When possible, standard ASTM tests were used to
10 determine the cured compound physical properties (see Table 2). Stress/strain properties (tensile strength, elongation at break, modulus values, energy to break) were measured at room temperature using an Instron 4202. Shore A hardness was measured at room temperature by using a Zwick Duromatic. The error (2σ) in measuring 100% Modulus is ± 0.11 MPa units; the error (2σ) in measuring
15 elongation is ± 13 % units.

The values "MH" and "ML" used here and throughout the description refer to "maximum torque" and "minimum torque", respectively. The "MS" value is the Mooney scorch value, the "ML(1+4)" value is the Mooney viscosity value. The
20 error (2σ) in the later measurement is ± 0.65 Mooney viscosity units. The values of "Tc" are cure times in minutes, and "Ts" is scorch time" in minutes.

Molecular weight of the PARAPOL™ polybutene processing oil was determined by gel permeation chromatography, and the values of number average
25 molecular weight (M_n) obtained have an error of $\pm 20\%$. The techniques for determining the molecular weight (M_n and M_w) and molecular weight distribution (MWD) are generally described in US 4,540,753 to *Cozewith et al.* and references cited therein, and in *Verstrate et al.*, 21 MACROMOLECULES 3360 (1988). In a typical measurement, a 3-column set is operated at 30°C. The elution
30 solvent used may be stabilized tetrahydrofuran (THF), or 1,2,4-trichlorobenzene (TCB). The columns are calibrated using polystyrene standards of precisely

known molecular weights. A correlation of polystyrene retention volume obtained from the standards, to the retention volume of the polymer tested yields the polymer molecular weight. The viscosity of the PARAPOL™ polybutene processing oil (Table 1) was determined as per ASTM D445-97.

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Tensile measurements were done at ambient temperature on Instron Series IX Automated Materials Testing System 6.03.08. Micro tensile specimens (dog-bone shaped) width of 0.08 inches (0.20 cm) and a length of 0.2 inches (0.5 cm) length (between two tabs) were used. The thickness of the specimens varied and was measured manually by Mitutoyo Digimatic Indicator connected to the system computer. The specimens were pulled at a crosshead speed of 20 inches/min. (51 cm/min.) and the stress/strain data was recorded. The average stress/strain value of at least three specimens is reported. The error (2σ) in tensile measurements is ± 0.47 MPa units.

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Adhesion was tested using a one-inch strip adhesion, wherein one inch x three inch adhesive bonds to Kraft paper are prepared. Samples are hung horizontally (in peel mode) in an air circulating oven and a 100 gram weight is suspended from the free end of the bond. The oven temperature is raised 10°F (4.1°C) every 15 minutes. The peel-fail temperature is the average of three readings.

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The error in the fatigue-to-failure values is $\pm 20\%$.

Oxygen permeability was measured using a MOCON OxTran Model 2/61 operating under the principle of dynamic measurement of oxygen transport through a thin film as published by *R.A. Pasternak et al.* in 8 JOURNAL OF POLYMER SCIENCE: PART A-2 467 (1970). The units of measure are cc-mil/m²-day-mmHg. Generally, the method is as follows: flat film or rubber samples are clamped into diffusion cells which are purged of residual oxygen using an oxygen free carrier gas. The carrier gas is routed to a sensor until a stable zero value is

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established. Pure oxygen or air is then introduced into the outside of the chamber of the diffusion cells. The oxygen diffusing through the film to the inside chamber is conveyed to a sensor which measures the oxygen diffusion rate.

5 Air permeability was tested by the following method. Thin, vulcanized test specimens from the sample compositions were mounted in diffusion cells and conditioned in an oil bath at 65°C. The time required for air to permeate through a given specimen is recorded to determine its air permeability. Test specimens were circular plates with 12.7-cm diameter and 0.38-mm thickness. The error (2σ) in
10 measuring air permeability is ± 0.245 ($\times 10^8$) units. Other test methods are described in Table 2.

Examples

 Compositions 1-15 (Tables 3-5) exemplify the benefits of incorporating
15 polybutene processing oil into blends of isobutylene copolymers comprising a halomethylstyrene moiety. Compositions 1, 6, and 11 represent copolymers of halogenated poly(isobutylene-*co-p*-methylstyrene) comprising various amounts of halogenation and amounts of *p*-methylstyrene (PMS) (see Table 3). The compositions incorporating PARAPOL™ have improved air permeability, while
20 improving or maintaining the processing properties such as green strength and fatigue to failure ratio values (Tables 6-8).

 Compositions 16-21 (Table 9) exemplify the benefits of incorporating polybutene processing oil into blends of an isobutylene-based polymer such as
25 HSSB with another rubber such as natural rubber, and an exfoliating clay. Composition 16 is the HSSB alone (SBB-6222, 100 phr), and Composition 17 is with natural rubber and PARAPOL™ alone (90 phr SBB, 10 phr natural rubber). Typically, halogenated rubbers such as HSSB have desirably low air permeability compared to, for example, natural rubber alone. When natural rubber is added to
30 these compositions, it is known that the air permeability goes up, such as disclosed

in *Inner Liners for High Performance Tires*, C.W. van Hellens in PROCEEDINGS OF RUBBER DIVISION, AMERICAN CHEMICAL SOCIETY (Indianapolis, Indiana, May 1984), and in *Bromobutyl and Chlorobutyl: A Comparison of Their Chemistry, Properties and Uses*, W. Hopkins, R.H. Jones, J. Walker in INTERNATIONAL
5 RUBBER CONFERENCE PROCEEDINGS 205 (Kyoto, October 1985). However, as seen in composition 17, when the polybutene is present, the air permeability is maintained or improved, even when natural rubber is present in the composition.

The addition of exfoliating clays can further improve air permeability of
10 these halogenated elastomeric compositions. Compositions 18-21 incorporate various amounts of an exfoliating clay. These data show that natural rubber improves the processing of the HSSB (Tables 10A and 10B). Further improvement in air permeability (lower values) are achieved upon addition of the clay and PARAPOL™. The inclusion of a naphthenic oil (CALSOL™) in
15 composition 19 actually disadvantageously increases air permeability of the blend.

Compositions 22-23 (Table 11) exemplify the benefits of incorporating polybutene processing oil into an elastomeric blend of a natural rubber, isobutylene copolymers comprising a halomethylstyrene moiety, and an
20 exfoliating clay. These data show that the processing properties are improved or maintained, while the air permeability is lowered upon addition of PARAPOL™.

Compositions 24-28 (Table 12) further exemplify the benefits of incorporating polybutene processing oil into an elastomeric blend of a natural
25 rubber, isobutylene copolymers comprising a halomethylstyrene moiety, and an exfoliating clay. Again, PARAPOL™ processing oil, polybutene, improves the air barrier properties of the blends, while maintaining or improving the processing properties. For example, the fatigue to failure values of the composition improves upon addition of PARAPOL™, as does the green strength (Tables 13A and 13B).
30 Compositions 27 and 28 represent preferred elastomeric blends having the lowest

air permeability values, wherein EXXPRO™ 89-4 is present with SBB-622 and natural rubber and PARAPOL™.

5 Compositions 29-44 exemplify the benefits of incorporating polybutene processing oils in various blends of isobutylene-based copolymers. The compositions 29-32 are blends of brominated butyl rubber (Bromobutyl 2222) with PARAPOL™ with and without clays. These data show that the addition of PARAPOL™ to compositions with (composition 31) and without (composition 30) an exfoliating clay improve the processing properties such as the fatigue-to-
10 failure values, while improving the air permeability values. The composition with both clay and polybutene are improved relative to the other brominated butyl rubber compositions.

 Compositions 33-36 exemplify the use of EXXPRO™ elastomers having
15 a PMS level of 5 wt% relative to the copolymer as a whole. These data show that the addition of polybutene processing oil alone (composition 34) improves the air barrier qualities of the blend, and adding an exfoliating clay alone (composition 35) improves the air barrier qualities. The addition of both the polybutene processing oil and clay (composition 36) improves the air barrier qualities. The
20 processing properties are improved for the 5 wt% PMS EXXPRO™ blends when the polybutene and clay (alone or together) are present, as evidenced by, for example, the green strength values and the fatigue-to-failure values.

 Compositions 37-40 exemplify the use of EXXPRO™ elastomers having
25 a PMS level of 7.5 wt% relative to the copolymer as a whole. Overall, the air permeability improves upon addition of PARAPOL™ and/or an exfoliating clay. Finally, compositions 41-44 exemplify the use of EXXPRO™ elastomers having a PMS level of 12 wt% relative to the copolymer as a whole. Again, the air permeability improves upon addition of the polybutene PARAPOL™ and/or an
30 exfoliating clay, as well as the processing properties. Also, the fatigue-to-failure

values in the 12 wt% PMS copolymer are improved relative to the 7.5 wt% PMS copolymers.

The inclusion of polybutene to the bromobutyl rubber and brominated poly(isobutylene-*co-p*-methylstyrene) and nanoclay compositions tend to improve the air permeability, as shown by compositions 29-44 in Table 15B. In one embodiment, the air permeability (at 65°C) ranges from 1.20×10^{-8} to 1.90×10^{-8} cm³-cm/cm²-sec-atm for these compositions, and from 1.30×10^{-8} to 1.8×10^{-8} cm³-cm/cm²-sec-atm in another embodiment.

Overall, the inclusion of polybutene process oils having a number average molecular weight from 400 to 6000 in one embodiment, and a viscosity of from 10 to 10,000 cSt at 100°C in another embodiment, have improved green strength and improved or maintained processability, as well as improved (lowered) air permeability. For example, the inclusion of polybutene in compositions of elastomers improves (increases) the fatigue-to-failure values. In particular, the fatigue-to-failure ratios improve when polybutene is added to elastomer/nanoclay compositions.

In one embodiment of the elastomeric nanocomposite compositions, where the elastomer is bromobutyl rubber, the unaged fatigue-to-failure values are greater than 40,000 units, and greater than 50,000 in another embodiment, and greater than 60,000 in yet another embodiment. In another embodiment, where the elastomer is a brominated poly(isobutylene-*co-p*-methylstyrene), the fatigue-to-failure values are greater than 70,000, and greater than 80,000 in another embodiment. The increase in the fatigue-to-failure values upon incorporation of polybutene into the compositions is particularly advantageous when clays are present, as these values tend to decrease upon addition of clays to an elastomer. In another embodiment of the elastomeric compositions, the green strength is greater than 45 units, and greater than 50 units in another embodiment. These values, of

course, may be further improved by changing the amounts of the various components in the compositions, or the viscosity and/or molecular weight of the polybutene.

5 Embodiments of the final nanocomposite of the present invention are useful as air barriers, such as used in producing innerliners, or innertubes for motor vehicle tires, or hoses for motor vehicles. In particular, the nanocomposites are useful in innerliners in articles such as truck tires, bus tires, passenger automobile, motorcycle tires, off the road tires, and the like. The improved heat
10 aging resistance of the present innerliner composition makes it particularly suited for use in truck tires to increase the retreading capability of the tire.

 While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will
15 appreciate that the invention lends itself to many different variations not illustrated herein. For these reasons, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

20 All priority documents are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted. Further, all documents cited herein, including testing procedures, are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted.

TABLE 2. Test Methods

Parameter	Units	Test
Mooney Viscosity (BIMS polymer)	ML 1+8, 125°C, MU	ASTM D 1646 (modified)
Mooney Viscosity (composition)	ML 1+4, 100°C, MU	ASTM D 1646
Air permeability	cm ³ -cm/cm ² -sec-atm	See text
Brittleness	°C	ASTM D 746
Green Strength (100% Modulus)	PSI	ASTM D 412
Mooney Viscosity (compound)	ML1+4, 100° C,MU	ASTM D 1646
Mooney Scorch Time	T _S 5, 125°C, minutes	ASTM D 1646
Oscillating Disk Rheometer (ODR) @ 160° C, ± 3°arc ML MH T _S 2 T _C 90 Cure rate	deciNewton.meter dNewton.m minute minute dN.m/minute	ASTM D 2084
Physical Properties press cured T _c 90+2 min @ 160°C Hardness Modulus 100% Tensile Strength Elongation at Break	Shore A MPa MPa %	ASTM D 2240 ASTM D 412 die C
Hot Air Aging, 72 hrs. @ 125°C Hardness Change Tensile Change Elongation Change Weight Change	% % % %	ASTM D 573
Tear Strength Die B & Die C	N/mm	ASTM D 624
Fatigue to Failure	cycles	ASTM 4482 using Cam 24 (136% extension)

Table 3. Components and Commercial Sources

Component	Brief Description	Commercial Source
BENTON™-34	Dimethylditallowammonium chloride modified montmorillonite clay	Elementis Specialties (Belleville, NJ)
Bromobutyl 2222	Brominated Poly(isobutylene-co-isoprene), Mooney Viscosity (1+8, 125°C) of from 27-37 MU	ExxonMobil Chemical Company (Houston, TX)
CALSOL™ 810	Naphthenic Oil ASTM Type 103	R.E. Carroll, Inc (Trenton, NJ)
CAPTAX™	2-mercaptobenzothiazole	R.T. Vanderbilt
CLAYTONE™-40	Dimethylditallowammonium chloride modified montmorillonite clay	Southern Clay Products (Gonzalez, TX)
CLOISITE™-25	Dimethylditallowammonium chloride modified montmorillonite clay	Southern Clay Products (Gonzalez, TX)
ESCOREZ™	Aromatic modified aliphatic resin, 95°C softening point	ExxonMobil Chemical Company (Houston, TX)
EXXPRO™ 3035	5 wt% PMS, 0.5 mol% BrPMS, Mooney Viscosity 40-50.	ExxonMobil Chemical Company (Houston, TX)
EXXPRO™ 89-4	5 wt% PMS, 0.75 mol% BrPMS, Mooney viscosity of 45±5 MU (1+8, 125°C)	ExxonMobil Chemical Company (Houston, TX)
EXXPRO™ 01-4	7.5 wt% PMS, 0.85 mol% BrPMS, Mooney viscosity of 45±5 MU (1+8, 125°C)	ExxonMobil Chemical Company (Houston, TX)
EXXPRO™ 96-4	12 wt% PMS, 0.85 mol% BrPMS, Mooney viscosity of 45±5 MU (1+8, 125°C)	ExxonMobil Chemical Company (Houston, TX)
KADOX™ 930	High Purity French Process Zinc Oxide	Zinc Corp. of America (Monaca, Pa)
Maglite-K	vulcanizer	C.P. Hall (Chicago, IL)
PARAPOL™	C ₄ raffinate	ExxonMobil Chemical Company (Houston, TX)
Rosin Oil MR-1085 A	tackifier	Sovereign Chemical (Akron, OH)
SP-1068	Brominated phenol-formaldehyde resin	Schenectady International (Schenectady, NY)
SBB	Star-branched butyl rubber 6222	ExxonMobil Chemical Company (Houston, TX)
Stearic acid	Cure agent	e.g., C.K. Witco Corp. (Taft, LA)
Sulfur	cure agent	e.g., R.E. Carroll (Trenton, NJ)
TMTD	tetramethylthiuram disulfide	e.g., R.T. Vanderbilt (Norwalk, CT)
Zinc Oxide 911, 720-C	activators	C.P. Hall (Chicago, IL)

Table 3. Components of Comparative and Example Compositions 1-5

Component (phr)	1	2	3	4	5
EXXPRO™ 89-4 (5 wt% PMS, 0.75 mol% BrPMS)	100.00	100.00	100.00	100.00	100.00
Carbon Black N660	60.00	60.00	60.00	60.00	60.00
CALSOL™-810	8.00	-	-	-	-
STRUKTOL™ -40MS	7.00	7.00	7.00	7.00	7.00
SP-1068	2.00	2.00	2.00	2.00	2.00
ESCOREZ™-2510	2.00	2.00	2.00	2.00	2.00
Stearic Acid	1.00	1.00	1.00	1.00	1.00
PARAPOL™-700	-	8.00	-	-	-
PARAPOL™-950	-	-	8.00	-	-
PARAPOL™-1300	-	-	-	8.00	-
PARAPOL™-2400	-	-	-	-	8.00
Zinc Oxide 911	1.00	1.00	1.00	1.00	1.00
MBTS	1.25	1.25	1.25	1.25	1.25
Sulfur	0.50	0.50	0.50	0.50	0.50

Table 4. Components of Comparative and Example Compositions 6-10

Component (phr)	6	7	8	9	10
EXXPRO™ 01-4 (7.5 wt% PMS, 0.85 mol% BrPMS)	100.00	100.00	100.00	100.00	100.00
Carbon Black N660	60.00	60.00	60.00	60.00	60.00
CALSOL™-810	8.00	-	-	-	-
STRUKTOL™ -40MS	7.00	7.00	7.00	7.00	7.00
SP-1068	2.00	2.00	2.00	2.00	2.00
ESCOREZ™-2510	2.00	2.00	2.00	2.00	2.00
Stearic Acid	1.00	1.00	1.00	1.00	1.00
PARAPOL™-700	-	8.00	-	-	-
PARAPOL™-950	-	-	8.00	-	-
PARAPOL™-1300	-	-	-	8.00	-
PARAPOL™-2400	-	-	-	-	8.00
Zinc Oxide 911	1.00	1.00	1.00	1.00	1.00
MBTS	1.25	1.25	1.25	1.25	1.25
Sulfur	0.50	0.50	0.50	0.50	0.50

Table 5. Components of Comparative and Example Compositions 11-15

Component (phr)	11	12	13	14	15
EXXPRO™ 96-4 (12 wt% PMS, 0.85 mol% BrPMS)	100.00	100.00	100.00	100.00	100.00
Carbon Black N660	60.00	60.00	60.00	60.00	60.00
CALSOL™-810	8.00	-	-	-	-
STRUKTOL™ -40MS	7.00	7.00	7.00	7.00	7.00
SP-1068	2.00	2.00	2.00	2.00	2.00
ESCOREZ™-2510	2.00	2.00	2.00	2.00	2.00
Stearic Acid	1.00	1.00	1.00	1.00	1.00
PARAPOL™-700	-	8.00	-	-	-
PARAPOL™-950	-	-	8.00	-	-
PARAPOL™-1300	-	-	-	8.00	-
PARAPOL™-2400	-	-	-	-	8.00
Zinc Oxide 911	1.00	1.00	1.00	1.00	1.00
MBTS	1.25	1.25	1.25	1.25	1.25
Sulfur	0.50	0.50	0.50	0.50	0.50

Table 6. Properties of Compositions 1-5

Property	1	2	3	4	5
Mooney scorch @ 135°C, T5, min.	20.47	21.85	21.40	22.22	22.32
Mooney viscosity @ 100°C	69.1	71.8	71.9	72.4	72.0
ODR, 3° Arc @ 160°C					
MH-ML	26.98	25.74	25.29	25.44	25.40
ML	13.17	14.48	14.51	14.54	15.15
MH	40.15	40.22	39.80	39.98	40.55
Ts2, min.	5.04	5.44	5.52	5.43	5.95
Tc50, min.	9.05	10.03	9.98	10.23	10.51
Tc90, min.	14.22	15.67	15.46	16.13	16.45
Hardness, Shore A	56	57	57	53	52
Aged Hardness (72 h @ 125°C)	65	61	61	62	57
100% Modulus, MPa	1.81	1.69	1.85	2.03	1.87
300% Modulus, MPa	5.63	5.63	6.00	6.20	6.13
Tensile, MPa	9.89	10.33	10.10	10.85	10.89
Elongation, %	702%	730%	676%	729%	694%
Aged 100% Modulus, MPa	3.06	2.29	2.54	2.72	2.68
Aged 300% Modulus, MPa	8.29	7.16	7.38	7.55	7.75
Aged Tensile, MPa	10.43	10.26	10.32	11.02	11.03
Aged Elongation, %	500%	555%	555%	617%	546%
Adhesion @ RT (Self-Carcass), N/mm	31.70	32.18	31.81	31.22	31.97
Adhesion @ 100°C (Self-Carcass), N/mm	22.16	21.55	24.96	29.63	24.11
Green Strength, Modulus @ 100% PSI	49.01	53.65	55.25	56.70	55.68
Time to Decay 75%	3.10	3.78	3.46	4.56	3.72
Tear Resistance-N/mm	40.04	41.93	40.51	42.31	40.92
Aged Die-C Tear Resistance-N/mm	39.13	37.82	35.05	37.48	38.35
Fatigue to Failure	1.50E+05	1.66E+05	1.90E+05	1.08E+05	9.79E+04
Fatigue to Failure (Aged)	2.11E+04	3.68E+04	5.56E+04	3.50E+04	7.11E+04
Air Permeability-(To Air)-65°C, cm ³ -cm/cm ² -sec-atm (x 10 ⁸)	2.56	2.11	2.02	1.92	1.84

Table 7. Properties of Compositions 6-10

Property	6	7	8	9	10
Mooney scorch @ 135°C, T5	16.97	18.33	17.93	18.33	18.75
Mooney viscosity @ 100°C	67.0	68.5	70.4	69.0	70.1
ODR, 3° Arc @ 160°C, 60 min					
MH-ML	28.41	26.83	27.77	27.54	27.31
ML	13.89	14.40	15.36	14.81	12.91
MH	42.30	41.23	43.13	42.35	40.22
Ts2	4.49	4.80	4.78	4.64	4.88
Tc50	7.68	8.76	8.71	8.95	8.53
Tc90	11.15	13.11	13.13	13.66	12.58
Hardness, Shore A	56	55	57	58	59
Aged Hardness (72 h @ 125°C)	61	59	59	61	62
100% Modulus, MPa	1.97	1.98	1.78	1.91	1.81
300% Modulus, MPa	6.24	6.10	5.92	5.98	6.11
Tensile, MPa	10.36	10.68	10.41	9.60	10.91
Elongation, %	747%	756%	667%	621%	694%
Aged 100% Modulus, MPa	3.65	2.77	2.38	2.66	2.65
Aged 300% Modulus, MPa	9.48	7.91	7.45	7.78	8.01
Aged Tensile, MPa	11.22	10.55	10.24	10.98	11.20
Aged Elongation, %	480%	548%	476%	586%	527%
Adhesion @ RT (Self-Carcass), N/mm	32.11	32.21	31.34	30.54	32.85
Adhesion @ 100C (Self-Carcass), N/mm	25.75	19.45	25.00	20.08	24.02
Green Strength, Modulus @ 100% PSI	53.94	56.70	58.29	56.41	59.02
Time to Decay 75%	3.58	4.76	4.91	4.90	4.80
Tear Resistance-N/mm	40.87	39.02	39.06	38.62	40.97
Aged Die-C Tear Resistance-N/mm	35.51	37.26	34.79	35.78	36.83
Fatigue to Failure	1.51E+05	1.85E+05	1.09E+05	1.29E+05	1.53E+05
Fatigue to Failure (Aged)	5.29E+04	4.73E+04	4.13E+04	2.20E+04	3.03E+04
Air Permeability-(To Air)-65°C, cm ³ -cm/cm ² -sec-atm (x 10 ⁸)	2.37	2.07	1.84	1.58	1.73

Table 8. Properties of Compositions 11-15

Property	11	12	13	14	15
Mooney scorch @ 135°C, T5	19.17	20.48	20.80	20.87	20.05
Mooney viscosity @ 100°C	66.7	67.8	69.3	70.2	69.8
ODR, 3° Arc @ 160°C, 60 min					
MH-ML	27.42	26.67	27.05	24.81	27.13
ML	15.03	12.97	13.57	13.90	13.94
MH	42.45	39.64	40.62	38.71	41.07
Ts2	4.85	5.11	5.23	5.21	5.16
Tc50	9.15	9.76	9.91	9.52	9.86
Tc90	14.10	15.32	15.53	14.39	15.54
Hardness, Shore A	59	60	60	60	61
Aged Hardness (72 h @ 125°C)	65	61	66	66	65
100% Modulus, MPa	1.91	2.08	2.34	2.53	2.17
300% Modulus, MPa	6.01	6.50	6.86	7.22	7.00
Tensile, MPa	10.28	10.59	10.71	10.51	11.32
Elongation, %	668%	678%	638%	597%	633%
Aged 100% Modulus, MPa	3.60	3.33	3.32	3.55	3.48
Aged 300% Modulus, MPa	9.71	8.59	8.50	8.82	9.40
Aged Tensile, MPa	11.36	11.21	10.85	10.66	12.10
Aged Elongation, %	438%	480%	474%	435%	506%
Adhesion @ RT (Self-Carcass), N/mm	31.54	31.05	29.82	28.28	30.79
Adhesion @ 100°C (Self-Carcass), N/mm	24.30	19.34	18.65	25.14	21.23
Green Strength, Modulus @ 100% PSI	53.80	58.00	62.06	63.22	65.98
Time to Decay 75%	3.12	3.54	3.60	3.42	4.97
Tear Resistance-N/mm	37.66	41.98	37.40	37.98	38.48
Aged Die-C Tear Resistance-N/mm	32.93	35.08	34.17	33.39	34.43
Fatigue to Failure (Unaged)	1.12E+05	6.40E+04	9.00E+04	7.42E+04	5.62E+04
Fatigue to Failure (Aged)	1.23E+04	2.51E+04	2.03E+04	1.23E+04	2.55E+04
Air Permeability-(To Air)-65°C, cm ³ -cm/cm ² -sec-atm (x 10 ⁸)	2.48	2.03	1.98	2.07	1.82

Table 9. Components of Comparative and Example Compositions 16-21

Component (phr)	16	17	18	19	20	21
SBB-6222	100.0	90.0	80.0	80.0	80.0	80.0
Natural Rubber	-	10.0	20.0	20.0	20.0	20.0
Carbon black N660	60.0	60.0	55.0	55.0	55.0	55.0
CALSOL™ 810	14.0	-	-	7.0	-	-
Rosin Oil MR-1085 A	4.0	-	-	-	-	-
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0
SP-1068	-	4.0	4.0	4.0	4.0	4.0
STRUKTOL™ -40MS	-	7.0	7.0	-	7.0	7.0
PARAPOL™-2500	-	7.0	7.0	7.00	7.00	7.00
CLOISITE-25	-	-	5.00	5.00	-	-
Bentone-34	-	-	-	-	-	5.00
Claytone-40	-	-	-	-	5.00	-
ZINC OXIDE 720-C	3.00	3.00	3.00	3.00	3.00	3.00
MBTS	1.25	1.25	1.25	1.25	1.25	1.25
sulfur	0.10	0.10	0.10	0.10	0.10	0.10

Table 10A. Properties of Compositions 16-21

Property	16	17	18	19	20	21
Mooney scorch @ 135°C, T5	9.02	12.73	11.72	10.77	9.43	10.1
Mooney scorch @ 135°C, T10	10.35	15.80	17.43	15.67	15.57	15.9
Mooney viscosity (1+4) @100°C	41.20	57.00	47.30	34.90	43.30	48.80
ODR, 1° ARC, 150°C						
MH-ML	5.37	6.79	6.15	6.48	6.35	6.41
ML	3.69	5.95	5.21	3.98	4.86	5.31
MH	9.06	12.74	11.36	10.46	11.21	11.72
Ts2	4.08	7.22	10.07	8.89	9.32	8.22
Tc50	4.52	9.17	14.96	12.17	13.42	12.04
Tc90	8.52	16.14	25.24	21.82	24.62	22.29
Hardness, SHORE A	49	52	53	49	54	54
Aged Hardness, 120 Hrs@100°C	67	62	63	62	60	60
100% Modulus, MPa	1.24	1.06	1.25	0.94	1.20	1.39
300% Modulus, MPa	4.11	2.77	3.53	2.65	3.05	4.02
Tensile, MPa	7.90	8.14	8.34	7.13	8.6	7.87
Elongation, %	606	876	704	672	913	605
aged 100% Modulus, MPa	2.79	2.00	1.81	1.83	1.78	1.77
aged 300% Modulus, MPa	8.81	5.86	4.97	6.20	5.11	4.88
aged Tensile, MPa	10.62	8.56	7.73	8.03	8.04	7.33
aged Elongation, %	432	563	543	406	552	521
Fatigue to Failure (unaged)	1,500,000	547,849	464,640	122,194	422,545	135,413
Unaged Adhesion @ R.T.-(Self-Self)	20.85	24.08	16.79	11.74	15.77	22.72
Adhesion @100°C (Self-Self)	11.91	14.56	7.97	3.89	6.14	10.17
Adhesion @ RT (Self-Carcass)	4.59	17.61	14.41	8.92	11.25	14.89
Adhesion @ 100°C (Self-Carcass)	4.44	2.99	4.03	4.51	5.16	7.10

Table 10B. Properties of Compositions 16-21

Property	16	17	18	19	20	21
Green Strength, Modulus @ 100% PSI	44.23	59.16	55.68	43.21	66.41	67.43
Time to Decay 75% from strain end point min	2.81	9.10	9.38	6.79	14.85	24.57
Die B Tear Resistance-N/mm	47.74	48.27	49.93	39.86	50.04	47.61
Die C Tear Resistance-N/mm	25.01	30.38	28.38	20.87	27.20	27.39
Air Permeability, @ 65°C, cm ³ -cm/cm ² -sec-atm (x 10 ⁸)	3.31	2.49	2.86	3.57	2.66	2.78
N ₂ Permeability, @ 65°C, cm ³ -cm/cm ² -sec-atm (x 10 ⁸)	2.98	2.31	2.57	2.99	2.36	2.71
Brittleness, °C	-45	-37	-37	-44	-37	-41

Table 11. Components and Properties of Example Compositions 22-23

Component (phr)	22	23
EXXPRO™ 3035	80.00	80.00
Natural rubber	20.00	20.00
Carbon black N-660	35.00	35.00
CLAYTONE 40	5.00	5.00
CALSOL™ 810	7.00	-
PARAPOL™ 2400	-	7.00
Rosin oil	4.00	4.00
Stearic acid	1.00	1.00
KADOX™ 911	1.00	1.00
MBTS	1.25	1.25
sulfur	0.50	0.50
Property		
Mooney scorch @135C, T5, min.	10.30	10.65
Mooney scorch @135C, T10, min.	11.30	11.67
Mooney scorch@ 100°C	44.70	49.70
ODR @150°C, 1 degree arc		
MH-ML	6.60	6.18
ML	6.15	6.74
MH	12.75	12.92
Ts2, min.	5.96	6.67
Tc50, min.	7.87	8.51
Tc90, min.	17.46	18.34
Hardness, Shore A	38.50	39.10
100% Modulus, MPa	1.12	1.12
200% Modulus, MPa	1.55	1.58
300% Modulus, MPa	2.01	2.16
Tensile, MPa	3.90	4.66
Elongation, %	778.00	824.00
Green Strength, 100%Modulus- PSI	48.87	53.07
Time to Decay 75%	5.53	7.88
Air Permeability, @65°C, cm ³ -cm/cm ² -sec-atm (x 10 ⁸)	4.54	3.67

Table 12. Components of Example Compositions 24-28

Components (phr)	24	25	26	27	28
SBB-6222	100.0	80.0	60.0	40.0	20.0
EXXPRO™-89-4	-	-	20.00	40.00	60.00
Natural Rubber	-	20.0	20.0	20.0	20.0
Carbon black-N-660	60.0	50.0	55.0	55.0	55.0
CLOISITE-25	-	10.00	5.00	5.00	5.00
CALSOL™-810	14.0	-	-	-	-
Rosin Oil MR-1085 A	4.0	-	-	-	-
Stearic acid	1.0	1.0	1.0	1.0	1.0
SP-1068	-	4.0	4.0	4.0	4.0
STRUKTOL™-40MS	-	7.0	7.0	7.0	7.0
PARAPOL™-2500	-	7.00	7.00	7.00	7.00
ZINC OXIDE 720-C	3.00	3.00	3.00	3.00	3.00
MBTS	1.25	1.25	1.25	1.25	1.25
sulfur	0.10	0.10	0.10	0.10	0.10

Table 13A. Properties of Example Compositions 24-28

Property	24	25	26	27	28
Mooney scorch @135°C, T5, min.	9.02	11.42	5.55	3.68	1.82
Mooney scorch @135°C, T10, min.	10.35	16.73	8.55	4.72	2.53
Mooney scorch @100°C	41.20	43.8	53.7	65.5	90.4
ODR, ARC 1°, 150°C					
MH-ML	5.37	6.20	7.81	8.81	8.05
ML	3.69	5.23	6.38	7.85	9.69
MH	9.06	11.43	14.19	16.66	17.74
Ts-2	4.08	11.02	9.47	8.08	8.18
Tc-50	4.52	15.12	14.58	14.58	14.67
Tc-90	8.52	26.25	25.13	25.23	25.71
Hardness, Shore A	49	57	58	59	60
Aged Hardness, 120 hr@100°C	67	63	63	60	63
100% Modulus, MPa	1.24	1.28	1.49	2.17	2.47
300% Modulus, MPa	4.11	3.12	4.56	6.28	6.77
Tensile, MPa	7.90	6.99	9.33	10.29	9.15
Elongation, %	606	660	658	598	521
Aged 100% Modulus, MPa	2.79	1.87	2.12	2.74	2.89
Aged 300% Modulus, MPa	8.81	4.87	5.72	7.3	8.35
Aged Tensile, MPa	10.62	6.58	8.04	9.22	9.7
Aged Elongation, %	432	486	549	479	402
Fatigue-to-failure (unaged)	1,500,000	197,910	92,870	48,943	2,221
Adhesion @RT (Self-Self), N/mm	20.85	13.34	20.45	23.91	23.8
Adhesion @100°C (Self-Self), N/mm	11.91	4.13	7	8.42	7.45
Adhesion @RT (Self-Carcass), N/mm	4.59	10.02	11.9	11.25	9.74
Adhesion @100°C (Self-Carcass), N/mm	4.44	3.12	4.74	1.15	0.78

Table 13B. Properties of Example Compositions 24-28

Property	24	25	26	27	28
Green Strength, Modulus @100% PSI	44.23	62.93	70.18	94.83	119.19
Time to Decay 75% from strain end point min.	2.81	11.91	46.92	-	-
Die B Tear Resistance-N/mm	47.74	41.46	58.02	60.12	63.12
Die C Tear Resistance-N/mm	25.01	22.79	30.41	37.58	33.94
Air Permeability, @65°C, cm ³ -cm/cm ² -sec-atm (x 10 ⁸)	3.29	2.63	2.70	2.79	2.75
N ₂ Permeability, @65°C, cm ³ -cm/cm ² -sec-atm (x 10 ⁸)	2.97	2.96	2.74	1.86	2.19
Brittleness, °C	-45	-42	-42	-42	-41

Table 14. Components of Example Compositions 29-44

[illegible]

Table 15A. Properties of Compositions 29-44

Property	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44
Mooney scorch @ 135°C, T5	17.30	18.45	15.42	15.73	15.23	16.73	2.72	1.27	16.33	16.72	5.12	3.78	16.17	17.48	4.05	16.55
Mooney scorch @ 135°C, T10	20.10	21.52	19.13	19.18	18.23	19.77	3.22	1.83	19.42	19.55	6.27	4.53	19.38	20.78	4.88	19.35
Mooney viscosity (1+4) @ 100°C	59.3	63.0	58.3	61.4	68.8	72.1	81.4	109.9	68.3	71.0	70.6	77.7	67.9	70.6	71.6	67.2
ODR, 3° ARC, 160°C																
MH-ML	24.63	23.99	27.97	25.54	27.91	25.85	32.58	29.46	30.12	27.90	31.88	30.20	29.05	27.63	24.91	27.98
ML	9.76	10.52	9.88	10.89	12.87	14.76	17.84	21.29	11.40	13.36	13.54	16.72	12.12	13.85	14.05	12.72
MH	34.39	34.51	37.85	36.43	40.78	40.61	50.42	50.75	41.52	41.26	45.42	46.92	41.17	41.48	38.96	40.70
Ts2	2.00	2.00	4.32	4.41	4.27	4.68	4.75	4.46	3.63	4.10	4.24	4.79	4.15	4.36	4.20	4.21
Tc50	9.56	10.06	11.96	11.99	8.38	8.48	14.72	14.84	7.63	7.89	14.22	15.17	8.03	8.95	18.01	7.97
Tc90	20.72	19.35	21.60	20.82	13.03	12.76	29.32	30.62	11.70	11.92	29.10	31.18	12.48	14.39	45.37	12.86
Hardness, Shore A	46	49	52	52	51	53	56	56	57	56	57	60	56	56	59	52
Aged Hardness, 72 Hrs @ 125°C	61	59	65	61	64	62	64	59	68	63	68	63	67	64	65	65
100% Modulus, MPa	1.17	1.28	1.53	1.57	1.85	1.89	3.07	3.39	2.00	1.80	2.39	2.65	2.00	2.04	2.34	1.62
300% Modulus, MPa	4.32	4.27	5.22	5.38	6.07	6.06	9.15	10.15	6.03	5.94	7.09	8.06	5.95	6.27	7.18	5.70
Tensile, MPa	10.45	10.49	10.22	10.85	10.14	10.73	11.77	12.04	9.97	10.88	10.99	12.05	10.00	10.67	12.52	10.00
Elongation, %	712	757	644	662	651	738	469	398	675	707	619	598	676	675	659	701
Aged 100% Modulus, MPa	2.27	1.97	2.82	2.16	3.25	2.71	4.31	3.94	3.73	2.58	4.21	3.56	3.8	2.89	3.92	2.95
Aged 300% Modulus, MPa	6.72	5.87	7.18	6.21	9.61	7.79	11.68	11.42	9.63	7.91	10.32	9.72	9.92	8.2	10.13	8.84
Aged Tensile, MPa	8.66	8.45	8.53	8.03	11.19	11.23	12.58	13.77	10.97	10.82	11.49	12.13	11.02	10.83	12.37	10.89
Aged Elongation, %	480	572	443	523	462	566	374	418	455	520	428	479	408	514	462	467
Fatigue to Failure (Unaged)	31,437	56,984	24,986	53,965	106,159	85,362	17,298	12,471	80,001	123,851	107,148	74,309	104,171	59,696	102,587	181,028
Fatigue to Failure (Aged)	6,934	20,197	13,702	26,046	14,698	16,317	6,538	8,011	12,878	44,506	21,898	22,871	9,982	12,792	41,154	12,295
Unaged Adhesion @RT (Self-Carcass), N/mm	32.79	31.98	19.72	23.62	30.57	29.11	23.54	25.00	29.86	27.68	24.32	24.46	25.86	23.89	17.14	29.14
Unaged Adhesion @100°C (Self-Carcass), N/mm	19.10	18.33	8.66	10.55	17.98	17.77	10.30	10.72	19.25	17.17	9.56	12.25	14.77	14.46	7.59	16.30

Table 15B. Properties of Compositions 29-44

Property	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44
Green Strength, Modulus @ 100% PSI	37.70	41.91	44.52	52.20	49.30	56.26	104.69	87.29	48.00	57.13	64.09	86.42	52.93	59.60	82.65	61.34
Time to Decay 75% from strain end point min.	1.39	1.58	2.06	2.95	3.21	3.55	70.15	>5 min.	2.46	2.93	4.42	11.93	3.08	3.61	8.63	4.09
Die B Tear Resistance-N/mm	60.70	62.50	60.82	71.00	70.64	70.28	76.05	84.18	66.50	70.18	74.16	86.90	68.16	71.34	75.40	70.03
Aged Die B Tear Resistance-N/mm	57.93	57.02	56.84	53.23	72.86	71.52	79.24	77.52	68.91	69.33	76.10	82.22	66.98	71.54	82.59	71.30
Die C Tear Resistance-N/mm	35.00	37.02	33.25	35.49	39.67	38.66	41.30	35.52	37.36	39.78	38.53	40.84	36.93	41.95	37.64	39.90
Aged Die C Tear Resistance-N/mm	30.48	29.92	29.01	29.72	36.14	36.97	36.73	36.90	32.82	34.48	40.58	38.55	33.76	35.20	39.77	34.54
Air Permeability 65°C -1, cm ³ -cm/cm ² -sec-atm (x 10 ⁶)	2.04	1.59	1.68	1.42	1.75	1.43	1.55	1.45	1.67	1.53	1.65	1.21	1.74	1.35	1.32	1.53
Air Permeability 65°C -2, cm ³ -cm/cm ² -sec-atm (x 10 ⁶)	1.91	1.54	1.64	1.43	1.84	1.46	1.59	1.48	1.52	1.69	1.62	1.18	1.54	1.30	1.23	1.78
Average	1.98	1.57	1.66	1.43	1.80	1.45	1.57	1.47	1.60	1.61	1.64	1.20	1.64	1.33	1.28	1.66

CLAIMS

We claim:

- 5 1. An elastomeric composition comprising at least one random copolymer comprising a C₄ to C₇ isomonoolefin derived unit, at least one filler, and polybutene oil having a number average molecular weight greater than 400.
- 10 2. The composition of Claim 1, wherein the copolymer is selected from a halogenated poly(isobutylene-*co-p*-methylstyrene), halogenated star-branched butyl rubber, halogenated butyl rubber, and mixtures thereof.
- 15 3. The composition of Claim 1, also comprising a thermoplastic resin.
- 15 4. The composition of Claim 1, wherein the polybutene has a molecular weight of less than 10,000.
- 20 5. The composition of Claim 1, wherein the polybutene is present from 2 to 40 phr.
- 25 6. The composition of Claim 1, wherein the filler is selected from calcium carbonate, clay, mica, silica and silicates, talc, titanium dioxide, starch and other organic fillers such as wood flower, and carbon black, and mixtures thereof.
- 30 7. The composition of Claim 1, wherein the composition also includes an exfoliated clay selected from exfoliated natural or synthetic montmorillonite, nontronite, beidellite, volkonskoite, laponite, hectorite, saponite, sauconite, magadite, kenyaite, stevensite, vermiculite, halloysite, aluminate oxides, hydrotalcite, and mixtures thereof.

8. An innerliner for a tire comprising the composition of Claim 1.
9. An elastomeric composition comprising an at least one poly(isoolefin-*co-p*-methylstyrene), at least one filler, and polybutene oil having a number
5 average molecular weight greater than 400.
10. The composition of Claim 9, wherein the poly(isoolefin-*co-p*-methylstyrene) is a halogenated poly(isobutylene-*co-p*-methylstyrene).
10
11. The composition of Claim 10, wherein the halogenated poly(isobutylene-*co-p*-methylstyrene) has a *p*-bromomethylstyrene content of from 0.1 to 5 wt% based on the weight of the copolymer.
12. The composition of Claim 9, also comprising a thermoplastic resin.
15
13. The composition of Claim 9, wherein the polybutene has a molecular weight of from less than 10,000.
14. The composition of Claim 9, wherein the polybutene is present from 2 to 40 phr.
20
15. The composition of Claim 9, wherein the filler is selected from calcium carbonate, clay, mica, silica and silicates, talc, titanium dioxide, starch and
25 other organic fillers such as wood flower, and carbon black, and mixtures thereof.
16. The composition of Claim 9, wherein the composition also includes an exfoliated clay selected from exfoliated natural or synthetic montmorillonite, nontronite, beidellite, volkonskoite, laponite, hectorite,
30

saponite, sauconite, magadite, kenyaite, stevensite, vermiculite, halloysite, aluminate oxides, hydrotalcite, and mixtures thereof.

17. An innerliner for a tire comprising the composition of Claim 9.

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18. An elastomeric composition comprising an elastomer, a filler, and polybutene processing oil having a number average molecular weight of from 400 to 10,000.

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19. The composition of Claim 30, wherein the polybutene has a viscosity of from 10 to 6000 cSt at 100°C.

20. The composition of Claim 30, wherein the polybutene is present from 2 to 30 phr.

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21. The composition of Claim 30, wherein naphthenic oil is substantially absent.

22. An elastomeric composition comprising at least one random copolymer comprising a C₄ to C₇ isomonoolefin derived unit, carbon black, at least one exfoliated clay, and polybutene oil having a number average molecular weight greater than 400.

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23. The composition of Claim 22, wherein the copolymer is selected from a halogenated poly(isobutylene-*co-p*-methylstyrene), halogenated star-branched butyl rubber, halogenated butyl rubber, and mixtures thereof.

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24. The composition of Claim 22, also comprising a thermoplastic resin.

25. The composition of Claim 22, wherein the polybutene has a molecular weight of less than 10,000.
26. The composition of Claim 22, wherein the polybutene is present from 2 to 40 phr.
27. The composition of Claim 22, wherein the filler is selected from calcium carbonate, clay, mica, silica and silicates, talc, titanium dioxide, starch and other organic fillers such as wood flower, and carbon black, and mixtures thereof.
28. The composition of Claim 22, wherein the exfoliated clay is selected from exfoliated natural or synthetic montmorillonite, nontronite, beidellite, volkonskoite, laponite, hectorite, saponite, sauconite, magadite, kenyaite, stevensite, vermiculite, halloysite, aluminate oxides, hydrotalcite, and mixtures thereof.
29. An innerliner for a tire comprising the composition of Claim 22.
30. The composition of Claim 22, wherein the polybutene has a viscosity of from 10 to 6000 cSt at 100°C.
31. The composition of Claim 22, wherein the polybutene has a viscosity of from 35 to 5000 cSt at 100°C.
32. The composition of Claim 22, wherein naphthenic oil is substantially absent.
33. The composition of Claim 22, wherein the unaged fatigue-to-failure value of the composition is greater than 70,000 units.

34. An elastomeric composition comprising at least one elastomer, at least one filler, and polybutene processing oil having a number average molecular weight of from 400 to 10,000.

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35. The composition of Claim 36, wherein the polybutene has a viscosity of from 10 to 6000 cSt at 100°C.

36. The composition of Claim 36, wherein the polybutene is present from 2 to 30 phr.

10

37. The composition of Claim 36, wherein naphthenic oil is substantially absent.

38. The composition of Claim 36, wherein the elastomer is a copolymer of a C₄ to C₇ isoolefin and a *p*-methylstyrene derived units.

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39. The composition of Claim 36, wherein the elastomer is halogenated.

40. The composition of Claim 36, wherein the filler is carbon black.

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41. An air barrier made by the method of combining at least one random copolymer comprising a C₄ to C₇ isomonoolefin derived unit, at least one filler, and polybutene oil having a number average molecular weight greater than 400, and at least one cure agent; and curing the combined components.

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42. The air barrier of Claim 41, wherein the copolymer is selected from a halogenated poly(isobutylene-*co-p*-methylstyrene), halogenated star-branched butyl rubber, halogenated butyl rubber, and mixtures thereof.

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43. The air barrier of Claim 41, also comprising a thermoplastic resin.
44. The air barrier of Claim 41, wherein the polybutene has a molecular
5 weight of less than 10,000.
45. The air barrier of Claim 41, wherein the polybutene is present from 2 to 40
phr.
- 10 46. The air barrier of Claim 41, wherein the filler is selected from calcium
carbonate, clay, mica, silica and silicates, talc, titanium dioxide, starch and
other organic fillers such as wood flower, and carbon black, and mixtures
thereof.
- 15 47. The air barrier of Claim 41, wherein the composition also includes an
exfoliated clay selected from exfoliated natural or synthetic
montmorillonite, nontronite, beidellite, volkonskoite, laponite, hectorite,
saponite, sauconite, magadite, kenyaite, stevensite, vermiculite, halloysite,
aluminate oxides, hydrotalcite, and mixtures thereof.
- 20 48. The air barrier of Claim 41, wherein the polybutene has a viscosity of from
35 to 5000 cSt at 100°C.
49. The air barrier of Claim 41, wherein naphthenic oil is substantially absent.
- 25 50. The air barrier of Claim 41, wherein the unaged fatigue-to-failure value of
the barrier is greater than 40,000 units.
51. The air barrier of Claim 41, wherein the air permeability of the barrier is
30 from 1.2×10^{-8} to 4×10^{-8} cm³-cm/cm²-sec-atm at 65°C.

52. The air barrier of Claim 41, wherein the polybutene processing oil is a copolymer of isobutylene derived units and 1-butene derived units.

5 53. The air barrier of Claim 41, also comprising a secondary elastomer selected from natural rubbers, polyisoprene rubber, styrene butadiene rubber (SBR), polybutadiene rubber, isoprene butadiene rubber (IBR), styrene-isoprene-butadiene rubber (SIBR), ethylene-propylene rubber, ethylene-propylene-diene rubber (EPDM), polysulfide, nitrile rubber,
10 propylene oxide polymers, star-branched butyl rubber and halogenated star-branched butyl rubber, brominated butyl rubber, chlorinated butyl rubber, star-branched polyisobutylene rubber, star-branched brominated butyl (polyisobutylene/isoprene copolymer) rubber; isobutylene/methylstyrene copolymers such as isobutylene/meta-
15 bromomethylstyrene, isobutylene/bromomethylstyrene, isobutylene/chloromethylstyrene, halogenated isobutylene cyclopentadiene, and isobutylene/chloromethylstyrene and mixtures thereof.

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ning of each regular issue of the PCT Gazette.*

(54) Title: ELASTOMERIC COMPOSITION

(57) Abstract: The present invention is a composition including an isobutylene-based copolymer and polybutene. The copolymers may be mixed with an exfoliating compound and clay, the entire composition forming a nanocomposite. The clay may or may not have an additional exfoliating treatment present prior to mixing with the interpolymers. The composition of the invention has improved air barrier properties and processing properties, and is suitable as an air barrier. One embodiment of the invention is an elastomeric composition including at least one random copolymer of at least a C₄ to C₇ isomonoolefin derived unit, at least one filler, and polybutene oil having a number average molecular weight greater than 400. The copolymer may be selected from a halogenated poly(isobutylene-*co-p*-methylstyrene), a halogenated star-branched butyl rubber, or a halogenated butyl rubber, and mixtures thereof.



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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>WO 00 69966 A (EXXON CHEMICAL PATENTS INC) 23 November 2000 (2000-11-23)</p> <p>abstract; claims 1-38 page 5, line 10 page 9, line 14-23 page 10, line 1-10 page 11, line 1-15 page 17; table 1</p> <p style="text-align: center;">--- -/--</p>	<p>1-6, 8-15, 17-37, 41-46, 52</p>



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Patent family members are listed in annex.

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- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

14 January 2003

Date of mailing of the international search report

24. 01. 2003

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/42767

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>GB 2 299 337 A (ADCO PRODUCTS INC) 2 October 1996 (1996-10-02)</p> <p>abstract; claims 1-12 page 7, line 20-30 page 8, line 2-15 page 9, line 10-30 page 10, line 4-30</p> <p>----</p>	<p>1-6, 9-15, 18-21, 34-40</p>
X	<p>EP 0 992 538 A (ADVANCED ELASTOMER SYSTEMS) 12 April 2000 (2000-04-12)</p>	<p>1-6,8, 18-21, 34-37,40</p>
Y	<p>abstract; claims 1-18 page 2, line 58 page 3, line 35,56 page 5, line 14-18,29,49-52,39 page 7, line 55 page 8, line 34,57</p> <p>----</p>	<p>1-40</p>
Y	<p>WO 98 53000 A (EXXON CHEMICAL PATENTS INC) 26 November 1998 (1998-11-26) cited in the application abstract; claims 1-12 page 9, line 2 -page 10, line 8</p> <p>----</p>	<p>1-40</p>
X	<p>WO 97 14748 A (EXXON CHEMICAL PATENTS INC) 24 April 1997 (1997-04-24) abstract; claims 1-23 page 1, line 24 page 5, line 20 page 8, line 6,26 page 9, line 9-16 page 10, line 21 page 14, line 16; example 4</p> <p>----</p>	<p>22-30,32</p>
X	<p>EP 0 376 558 A (EXXON CHEMICAL PATENTS INC) 4 July 1990 (1990-07-04) abstract; claims 1-14 page 2, line 1-5 page 4, line 41-54 page 5, line 15-35 page 6, line 46-55 page 9, line 14-60; example 5</p> <p>-----</p>	<p>41-46, 48-52</p>

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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-21,34-40

An elastomeric composition or innerliner for tire comprising
A) a random copolymer comprising a C4 to C7 isomonoolefin derived unit or polyisooolefin-co-p-methylstyrene or elastomer
B) filler
C) polybutene oil

2. Claims: 22-33

Elastomeric composition comprising
A) a random copolymer comprising a C4 to C7 isomonoolefin derived unit
B) carbon black filler
C) exfoliated clay
D) polybutadiene oil.

3. Claims: 41-53

Air barrier made by combining
A) a random copolymer comprising a C4 to C7 isomonoolefin derived unit
B) one filler
C) polybutene oil
D) cure agent

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/42767

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